

Appln. No.:10/784,425

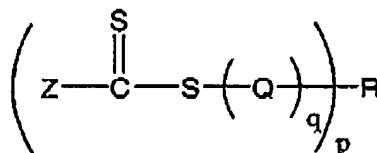
Docket. No. TW5922USDIV

Amendments to the Claims

This listing of claims will replace all prior versions, and listings, of claims in the application:

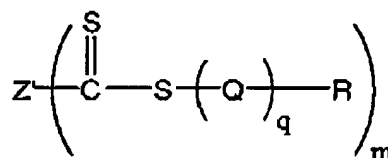
Listing of Claims:

1. (previously presented) A process for the synthesis of polymers selected from the group consisting of:



Formula A

and

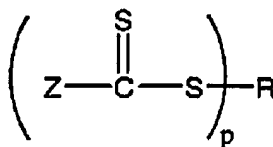


Formula B

comprising contacting:

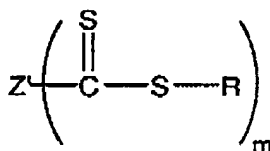
(i) one or more monomers selected from the group consisting of vinyl monomers of structure $\text{CH}_2=\text{CUV}$, maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers;

(ii) a thiocarbonylthio compound selected from the group consisting of:



Formula C

and



Formula D

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having a chain transfer constant greater than about 0.1; and

(iii) free radicals produced from a free radical source; and
controlling the polydispersity of the polymer being formed by varying the
ratio of the number of molecules of (ii) to the number of molecules of (iii);

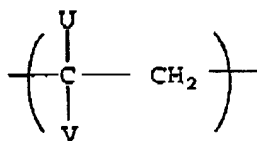
the polymer of Formula A being made by contacting (i), (ii)C and (iii)
and the polymer of Formula B being made by contacting (i), (ii) D and (ii);

wherein:

Z is selected from the group consisting of hydrogen, chlorine,
optionally substituted alkyl, optionally substituted aryl, optionally
substituted heterocyclyl, optionally substituted alkylthio, optionally
substituted alkoxy carbonyl, optionally substituted aryloxy carbonyl
(-COORⁿ), carboxy (-COOH), optionally substituted acyloxy (-O₂CRⁿ),
optionally substituted carbamoyl (-CONRⁿ₂), cyano (-CN), dialkyl- or
diaryl- phosphonato [-P(=O)(ORⁿ)₂], dialkyl- or diaryl-phosphinato [-
P(=O)Rⁿ₂], and a polymer chain formed by any mechanism;

Z' is a m-valent moiety derived from a member of the group
consisting of optionally substituted alkyl, optionally substituted aryl and a
polymer chain; where the connecting moieties are selected from the group
that consists of aliphatic carbon, aromatic carbon, and sulfur;

Q is selected from the group consisting of
repeating unit



and

repeating units from maleic anhydride, N-alkylmaleimide, N-arylmaleimide,
dialkyl fumarate and cyclopolymerizable monomers;

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U is selected from the group consisting of hydrogen, halogen, optionally substituted C₁-C₄ alkyl wherein the substituents are independently selected from the group that consists of hydroxy, alkoxy, aryloxy (OR^u), carboxy, acyloxy, aroyloxy (O₂CR^u), alkoxy-carbonyl and aryloxy-carbonyl (CO₂R^u);

V is selected from the group consisting of hydrogen, R^v, CO₂H, CO₂R^v, COR^v, CN, CONH₂, CONHR^v, CONR^v₂, O₂CR^v, OR^v and halogen;

R is selected from the group consisting of optionally substituted alkyl; an optionally substituted saturated, unsaturated or aromatic carbocyclic or heterocyclic ring; optionally substituted alkylthio; optionally substituted alkoxy; optionally substituted dialkylamino; an organometallic species; and a polymer chain prepared by any polymerization mechanism; in compounds C and D, R[•] is a free-radical leaving group that initiates free radical polymerization;

R^u is selected from the group consisting of optionally substituted C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, aryl, heterocyclyl, aralkyl, alkaryl wherein the substituents are independently selected from the group that consists of epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy and carboxylates, sulfonic acid and sulfonates, alkoxy- or aryloxy-carbonyl, isocyanato, cyano, silyl, halo, and dialkylamino;

q is 1 or an integer greater than 1;

p is 1 or an integer greater than 1; when p≥2 then R=R^p;

m is an integer ≥2; and

R^p is a p-valent moiety selected from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a

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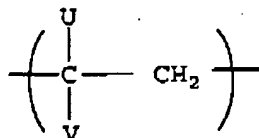
polymer chain; where the connecting moieties are selected from the group consisting of aliphatic carbon, aromatic carbon, silicon, and sulfur; in compounds C, R'• is a free radical leaving group that initiates free radical polymerization.

2. (previously presented) The process according to Claim 1 comprising controlling polydispersity by varying the ratio of the number of molecules of (ii) to (iii) as follows:

- (a) lower polydispersity by increasing the ratio of (ii) to (iii); and
- (b) increase polydispersity by decreasing the ratio of (ii) to (iii)

3. (previously presented) The process according to Claim 2 comprising increasing the ratio of (ii) to (iii) and obtaining a polymer having a polydispersity below about 1.5.

4. (previously presented) The process according to Claim 1 comprising selecting the following monomer repeating unit:



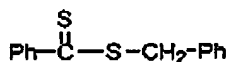
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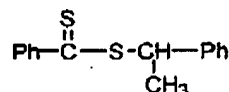
from (i).

5. (previously presented) The process according to Claim 1 comprising selecting the monomer units Q and the value of q so that when $q \geq 1$ and Q results from a single monomer species, then the polymer is homopolymer; when $q \geq 2$ and Q results from the selection from 2 or more different monomer species in irregular sequence then the polymer is copolymer; and when $q \geq 2$ and Q results from the selection from 2 or more different monomer species in which each different monomer or group of monomers appears in a discrete sequence then the polymer is block copolymer.

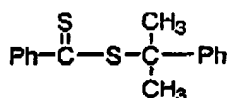
6. (previously presented) The process according to Claim 1 wherein the thiocarbonylthio compound is selected from the group consisting of:



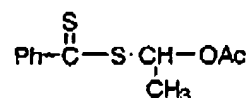
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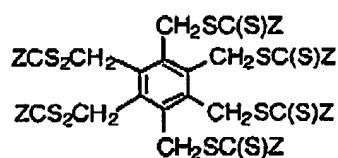
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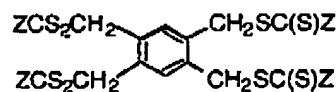
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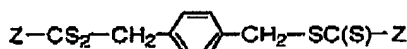
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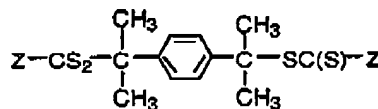
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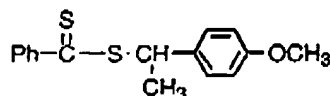
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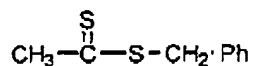
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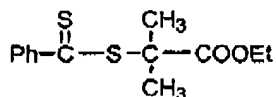
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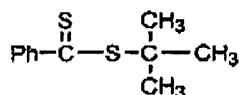
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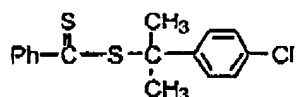
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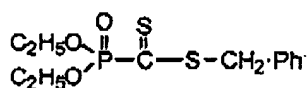
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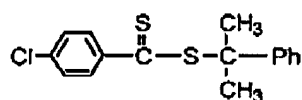
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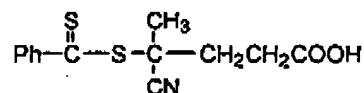
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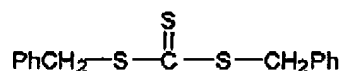
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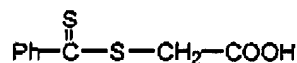
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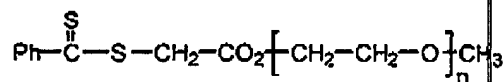
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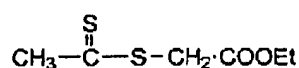


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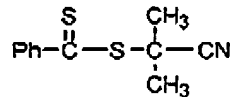


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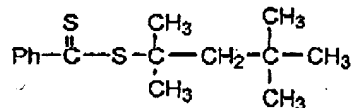
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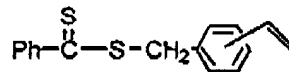
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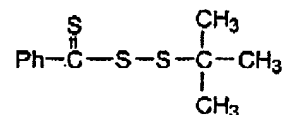
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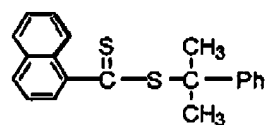
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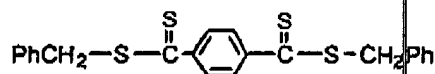
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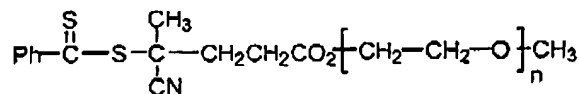
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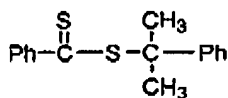
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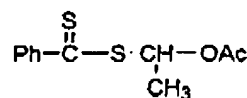
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wherein Z is phenyl.

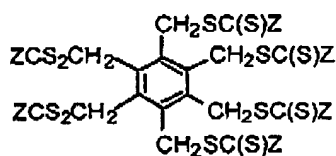
7. (original) A chain transfer agent selected from the group consisting of:



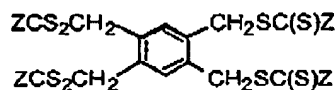
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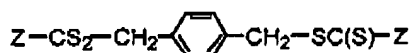
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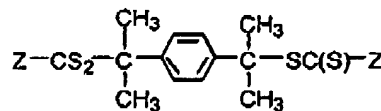
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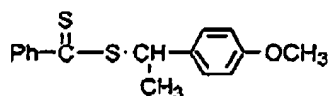
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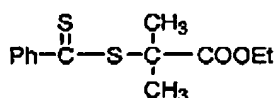
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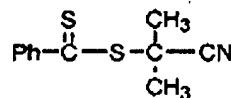
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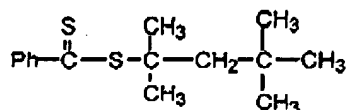
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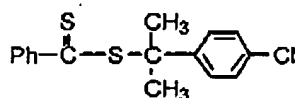
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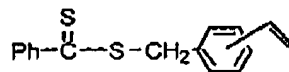
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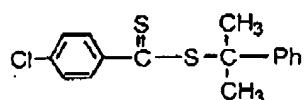
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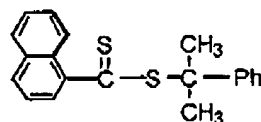
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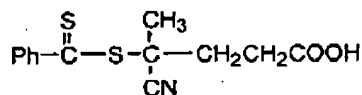
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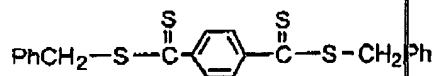
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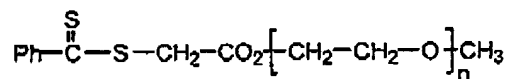
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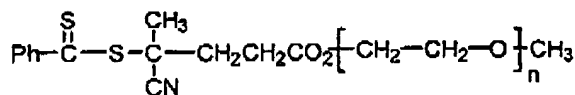


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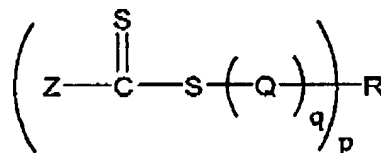
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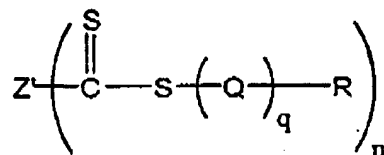
wherein Z is phenyl.

8. (previously presented) A polymer of the Formula



Formula A

and



Formula B

wherein:

Z is selected from the group consisting of hydrogen, chlorine, optionally substituted alkyl, optionally substituted aryl, optionally substituted heterocyclyl, optionally substituted alkylthio, optionally

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Z' is a m-valent moiety derived from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a polymer chain; where the connecting moieties are selected from the group that consists of aliphatic carbon, aromatic carbon, and sulfur;

repeating unit $\left(\begin{array}{c} \text{U} \\ | \\ -\text{C}- \\ | \\ \text{V} \end{array} \text{CH}_2 \right)$ and

U is selected from the group consisting of hydrogen, halogen, optionally substituted C₁-C₄ alkyl, wherein the substituents are independently selected from the group consisting of hydroxy, alkoxy, aryloxy (OR^u), carboxy, acyloxy, aryloxy (O₂CR^u), alkoxy-carbonyl and aryloxy-carbonyl (CO₂R^u);

R is selected from the group consisting of optionally substituted alkyl; an optionally substituted saturated, unsaturated or aromatic carbocyclic or heterocyclic ring; optionally substituted alkylthio; optionally substituted alkoxy; optionally substituted dialkylamino; an organometallic

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species; and a polymer chain prepared by any polymerization mechanism; R• being derived from a free radical leaving group that initiates free radical polymerization;

R" is selected from the group consisting of optionally substituted C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, aryl, heterocyclyl, aralkyl, alkaryl wherein the substituents are independently selected from the group that consists of epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy and carboxylates, sulfonic acid and sulfonates, alkoxy- or aryloxy-carbonyl, isocyanato, cyano, silyl, halo, and dialkylamino;

q is 1 or an integer greater than 1;

p is 1 or an integer greater than 1; when p≥2, then R=R';

m is an integer ≥2; and

R' is a p-valent moiety derived from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a polymer chain; where the connecting moieties are selected from the group consisting of aliphatic carbon, aromatic carbon, silicon, and sulfur; R'• being derived from a free radical leaving group that initiates free radical polymerization.

9. (previously presented) The polymer according to Claim 8 selected from the group consisting of random, block, graft, star and gradient copolymer.

10. (previously presented) The polymer according to Claim 9 having end group functionality.

11. (previously presented) The process of claim 1 wherein said polymer chain comprises condensation polymers or chain polymers.

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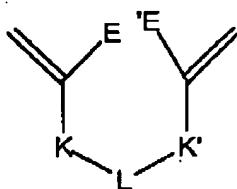
12. (previously presented) The process of claim 11 wherein said condensation polymers comprise polyesters, polycarbonates, poly(alkylene oxide)s, nylons or polyurethanes.

13. (previously presented) The process of claim 12 wherein said polyesters comprise polycaprolactones or polyethylene terephthalates.

14. (previously presented) The process of claim 11 wherein said chain polymers comprise poly(meth)acrylates or polystyrenics.

15. (previously presented) The process of claim 1 wherein said copolymerizable monomers comprise compounds containing two or more unsaturated links suitably disposed to allow propagation by a sequence of intramolecular and intermolecular additions steps that lead to incorporation of cyclic units in polymer backbone.

16. (previously presented) The process of claim 15 wherein said copolymerizable monomers comprise
1,6-dienes, substituted 1,6-heptadienes or monomers of the generic structure:



wherein E and E' are independently selected from the group consisting of H, CH₃, CN, COOAlkyl and Ph; K and K' are selected from the group consisting of CH₂, C=O, Si(CH₃)₂ and O; L is selected from the group consisting of C(E)₂, O, N(Alkyl)₂ salts, and P(O)Alkyl; and where K, K', L, E and E' are chosen such that said monomer undergoes cyclopolymerization.

17. (previously presented) The process of claim 1 wherein said vinyl

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monomers comprise acrylate and methacrylate esters, acrylic and methacrylic acids, styrenes, acrylamides, methacrylamides, methacrylonitriles, and mixtures thereof.

18. (previously presented) The process of claim 17 wherein said vinyl monomers further comprise mixtures with other monomers.

19. (previously presented) The process of claim 1, 17 or 18 wherein said vinyl monomers comprise methyl methacrylate, ethyl methacrylate, propyl methacrylate or isomers thereof, butyl methacrylate and isomers thereof, 2-ethylhexyl methacrylate, isobornyl methacrylate, methacrylic acid, benzyl methacrylate, phenyl methacrylate, methacrylonitrile, alpha-methylstyrene, methyl acrylate, ethyl acrylate, propyl acrylate or isomers thereof, butyl acrylate or isomers thereof, 2-ethylhexyl acrylate, isobornyl acrylate, acrylic acid, benzyl acrylate, phenyl acrylate, acrylonitrile, styrene, functional methacrylates, acrylates and styrenes selected from glycidyl methacrylate, 2-hydroxyethyl methacrylate, hydroxypropyl methacrylate or isomers thereof, hydroxybutyl methacrylate or isomers thereof, N,N-dimethylaminoethyl methacrylate, N,N-diethylaminoethyl methacrylate, triethyleneglycol methacrylate, itaconic anhydride, itaconic acid, glycidyl acrylate, 2-hydroxyethyl acrylate, hydroxypropyl acrylate and isomers thereof, hydroxybutyl acrylate and isomers thereof, N,N-dimethylaminoethyl acrylate, N,N-diethylaminoethyl acrylate, triethyleneglycol acrylate, methacrylamide, N-methylacrylamide, N,N-dimethylacrylamide, N-tert-butylmethacrylamide, N-n-butylmethacrylamide, N-methylolmethacrylamide, N-ethylolmethacrylamide, N-tert-butylacrylamide, N-n-butylacrylamide, N-methylolacrylamide, N-ethylolacrylamide, vinyl benzoic acid and isomers thereof, diethylaminostyrene and isomers thereof, alpha-methylvinyl benzoic acid and isomers thereof, diethylamino alpha-methylstyrene and isomers thereof, p-vinylbenzene sulfonic acid, p-vinylbenzene sulfonic sodium salt, trimethoxysilylpropyl methacrylate, triethoxysilylpropyl methacrylate, tributoxysilylpropyl methacrylate, dimethoxymethylsilylpropyl methacrylate, diethoxymethyl-silylpropylmethacrylate,

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dibutoxymethylsilylpropyl methacrylate, diisopropoxymethylsilylpropyl methacrylate, dimethoxysilylpropyl methacrylate, diethoxysilylpropyl methacrylate, dibutoxysilylpropyl methacrylate, diisopropoxysilylpropyl methacrylate, trimethoxysilylpropyl acrylate, triethoxysilylpropyl acrylate, tributoxysilylpropyl acrylate, dimethoxymethylsilylpropyl acrylate, diethoxymethylsilylpropyl acrylate, dibutoxymethylsilylpropyl acrylate, diisopropoxymethylsilylpropyl acrylate, dimethoxysilylpropyl acrylate, diethoxysilylpropyl acrylate, dibutoxysilylpropyl acrylate, diisopropoxysilylpropyl acrylate, vinyl acetate, vinyl butyrate, vinyl benzoate, vinyl chloride, vinyl fluoride, vinyl bromide, maleic anhydride, N-phenylmaleimide, N-butylmaleimide, N-vinylpyrrolidone, N-vinylcarbazole, butadiene, isoprene, chloroprene, ethylene, or propylene.

20. (previously presented) The process of claim 1 wherein substituents for R, R', Z, Z', U and V comprise epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy and carboxylates, sulfonic acid and sulfonates, alkylcarbonyloxy, isocyanato, cyano, silyl, halo or dialkylamino.

21. (previously presented) The process of claim 1 wherein substituents for R, R', Z, Z', U and V comprise alkoxy, alkyl or aryl.

22. (previously presented) The process of claim 1 wherein said heterocyclic ring comprises a ring structure containing 3 to 10 atoms at least one of which is selected from O, N and S.

23. (previously presented) The process of claim 1 wherein said polymer of the formula A or formula B is a end-functional polymer, block polymer, multiblock polymer, gradient polymer, star polymer, graft polymer or a branched polymer.

24. (previously presented) The process of claim 1 wherein said free radical source comprises thermal initiators, spontaneous generation from monomers, redox initiating systems, photochemical initiating systems or high energy radiation.

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25. (previously presented) The process of claim 24 wherein said thermal initiator comprises 2,2'-azobis(isobutyronitrile), 2,2'-azobis(2-cyano-2-butane), 4,4'-azobis(4-cyanopentanoic acid), 1,1'-azobis(cyclohexanecarbonitrile), dibenzoyl peroxide, or ammonium peroxydisulfate.
26. (previously presented) The process of claim 1, wherein said process is carried out at temperatures in the range of -20°C to 200°C.
27. (previously presented) The process of claim 1 wherein said process is carried out in emulsion, solution or suspension.
28. (previously presented) The process of claim 27 wherein said process is carried out in a batch, semi-batch, continuous or feed mode.
29. (previously presented) The process of claim 1, 24, 25, 26, 27 or 28 wherein said thiocarbonylthio compound is added before polymerization is commenced.
30. (previously presented) The process of claim 1, 24, 25, 26, 27 or 28 wherein polydispersity of said polymer of formula A or B is controlled by adding said thiocarbonylthio compound over the course of polymerization.
31. (previously presented) The process of claim 1, 24, 25, 26, 27 or 28 wherein said polymer of formula A or B having multimodal molecular weight distribution can be produced by adding said thiocarbonylthio compound over the course of polymerization.
32. (previously presented) The process of claim 1 wherein said process is carried out in emulsion or suspension.
33. (previously presented) The process of claim 32 wherein a reaction medium is water.

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34. (previously presented) The process of claim 1 wherein said process is carried out in a feed mode.

35. (previously presented) The process of claim 34 wherein said process comprises:

(i) charging a reactor with a medium and said thiocarbonylthio compound in a reactor; and

(ii) heating and stirring contents in said reactor while introducing in said reactor said monomers in said medium and said free radical source dissolved or suspended in said medium.

36. (previously presented) The process of claim 34 wherein said process comprises:

(i) charging a reactor with a medium and said thiocarbonylthio compound and a portion of said monomers in a reactor; and

(ii) heating and stirring contents in said reactor while introducing in said reactor a remaining portion of said monomers in said medium and said free radical source dissolved or suspended in said medium.

37. (previously presented) The process of claim 35 or 36 further comprising continuing heating of contents in said reactor for additional period after completing feeding of said free radical source and said monomers.

38. (previously presented) The process of claim 37 further comprising isolating said polymers of the formula A or B by stripping off said medium and unreacted said monomers.

39. (previously presented) A polymer of the formula A or B made by the process of claim 1.

40. (previously presented) A solution or emulsion of a polymer of the formula A or B made by the process of claim 1.

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41. (previously presented) The process of claim 1 wherein Z in said Formula C is a substituted alkylthio.

42. (previously presented) The process of claim 1 or 41 wherein R in said Formula C is a substituted alkylthio.

43. (previously presented) The process of claim 1 or 41 wherein R in said Formula C is a substituted alkyl.

44. (previously presented) The process of claim 43 wherein R in said Formula C is $-\text{C}(\text{Me})_2\text{C}_6\text{H}_4\text{Cl}$, $-\text{C}(\text{Me})_2\text{Ph}$, $-\text{C}(\text{Me})_2\text{COOEt}$, $-\text{C}(\text{Me})_2\text{CN}$, $-\text{C}(\text{Me})(\text{CH}_2\text{CH}_2\text{COOH})\text{CN}$, or $-\text{C}(\text{Me})(\text{CH}_2\text{CH}_2\text{COONa})\text{CN}$.

45. (previously presented) The process of claim 1 or 41 wherein R in said Formula C is a substituted alkylthio substituted with cyano.

46. (previously presented) The process of claim 1 or 42 wherein R in said Formula C is a substituted alkyl substituted with cyano.

47. (currently amended) The process of claim 41 wherein substituent ~~[[Z]]~~ in said substituted alkylthio is ~~substituted with~~ phenyl.

48. (currently amended) The process of claim 41 wherein ~~[[Z in]]~~ said substituted alkylthio is benzylthio.

49. (previously presented) The process of claim 48 wherein R is benzyl.

50. (previously presented) The process of claim 1 wherein said thiocarbonylthio compound is 4-cyanopentanoic acid dithiobenzoate or its sodium salt.

51. (previously presented) The process of claim 50 wherein medium is water.

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52. (previously presented) A coating composition, compatibiliser, thermoplastic elastomer, dispersing agent, rheology control agent, photoresist, engineering plastic, adhesive, or a sealant comprising polymers made by the process of claim 1.

53. (previously presented) A coating composition comprising polymers made by the process of claim 1.

54. (previously presented) The coating composition of claim 53 comprising pigments, durability agents, corrosion and oxidation inhibitors, rheology control agents, or metallic flakes.

55. (previously presented) The coating composition of claim 53 or 54 wherein said composition is suitable for producing clear coats or paints for automobile or maintenance finishes.

56. (previously presented) A composition comprising polymers of Claim 3.

57. (previously presented) The composition of claim 56 wherein said composition is a coating composition, compatibiliser, thermoplastic elastomer, dispersing agent, rheology control agent, photoresist, engineering plastic, adhesive, or a sealant.

58. (previously presented) The polymers of claim 8 wherein Q results from styrene and butadiene monomers.

59. (previously presented) A composition comprising the polymers of claim 58.